

Measurements of CsI Band-Gap Closure to 93 GPa

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Infrared-absorption measurements to a peak pressure of 93 GPa document the pressure-induced closure of the band gap of CsI to about 4450 cm^{-1} (0.55 eV). In accord with previous spectroscopic measurements to 60 GPa, our data show that the band gap of CsI decreases continuously with pressure, and metallization (complete closure of the gap) is expected to occur above 100 GPa. A recent claim that CsI becomes metallic at 65 ± 5 GPa is therefore spurious.

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The high-pressure optical properties of CsI have been recently investigated as a means of constraining the pressure at which the salt undergoes band-overlap metallization.¹⁻⁶ Detailed absorbance studies have been conducted on both monocrystalline^{4,5} and polycrystalline¹⁻³ samples of CsI; three independent studies document an absorption-edge energy of between 1.54 and 1.70 eV at 60 GPa, with a rate of decrease in energy of about 0.05 eV/GPa. Thus, the recent claim by Vohra *et al.*⁶ that CsI at 62 GPa has a band gap of less than 0.36 eV, and metallizes at 65 ± 5 GPa, implies a dramatic drop in the band-gap energy within a narrow pressure interval. If correct, this last study would represent the first observation of pressure-induced metallization in an alkali-metal halide. In order to constrain the metallization pressure of CsI more accurately, we have carried out a Fourier-transform infrared spectroscopic (FTIR) study with which we characterize the shift in the absorption edge of CsI to higher pressures (peak of 93 GPa) and lower energies than have previously been documented. In this work we report the highest-pressure infrared absorption spectra that have been collected to date.⁷⁻⁹

In our experiment, polycrystalline cesium iodide of 99.9% purity (Alfa Ventron Corp.) was compressed in a Mao-Bell-type diamond cell¹⁰ using type-I diamonds with 200- μm culets. Gaskets made both of Inconel X750 (0-60 GPa) and of spring steel (0-98 GPa) were used to contain samples approximately 80 μm in diameter. Samples are estimated to be near 10 μm in thickness. Pressure was measured at four to eight points on each sample with use of the ruby fluorescence technique,¹¹ and variations in pressure were approximately $\pm 5\%$ -7% from the average sample pressure. Absorption spectra were measured at room temperature with the use of a Bomem DA3.010 interferometer with a liquid-N₂-cooled InSb detector, a CaF₂ beam splitter, and a globar source. Spectra were recorded between 1700 and 9100 cm^{-1} , but two-phonon absorption of diamond obscures the spectra below 2600 cm^{-1} . Our spectra were collected with 4- cm^{-1} resolution, and are reported with a resolution of 64 cm^{-1} (8×10^{-3} eV).

Representative spectra between average pressures of 56 and 89 GPa are shown in Fig. 1. With recognition of the fact that absorbances above about 4.4 represent no measurable transmittance in our experiments, a minimum energy for the absorption edge at each pressure is determined from the highest frequency at which transmitted radiation is observed. As with previous polycrystalline absorption measurements,¹⁻³ we do not resolve an excitonlike peak,^{4,5} possibly because of the effects of pressure gradients or optical anisotropy of the samples.³ Although no quantitative measurements of the absorption edge were performed below 56 GPa, we observe color changes characteristic of the band gap moving through the visible region of the spectrum: Our samples appear yellow in transmitted light at pressures of about 35 GPa, and steadily redden until becoming opaque to transmitted visible

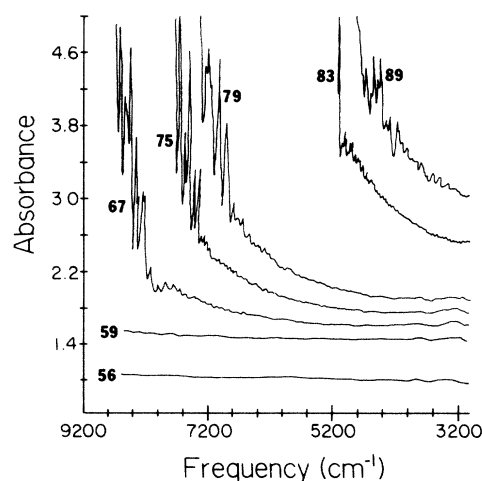


FIG. 1. 300-K infrared-absorption spectra of CsI; bold numbers represent the average sample pressure in gigapascals. All spectra are plotted on the same absorbance scale. Because CsI recrystallizes as the sample pressure is changed, the increase in the base-line absorbance is interpreted as being due to increased grain-boundary scattering at very high pressures. Small, impurity hydroxyl bands are visible between 3200 and 4000 cm^{-1} in the lower-pressure spectra.

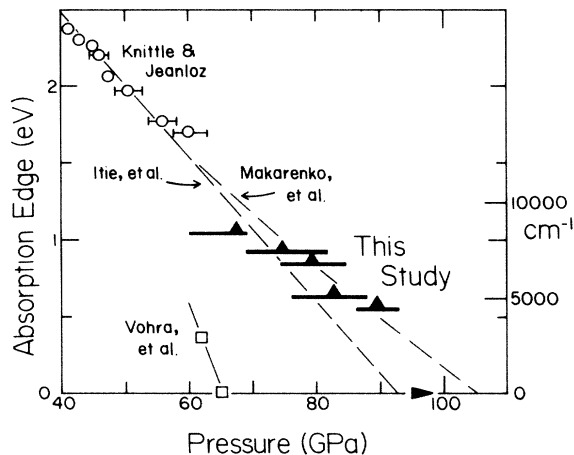


FIG. 2. Absorption-edge energy vs pressure for CsI. Bars represent the absolute pressure variation in each sample, while dark triangles represent our best estimate of the average sample pressure, and denote that our measurements of the edge energy are a minimum estimate (see text). The arrow at zero energy indicates our highest-pressure visual observation. The band-gap determinations of Vohra *et al.* (Ref. 6) are shown by squares. Previous data of Knittle and Jeanloz (Refs. 2 and 3) are plotted as open circles; Makarenko, Goncharov, and Stishov (Ref. 4) and Itie, Polian, and Besson (Ref. 5) obtained essentially coincident data to pressures of 60.3 and 57.5 GPa, respectively. Extrapolations of the previous data to zero energy by Itie, Polian, and Besson (Ref. 5) and Makarenko, Goncharov, and Stishov (Ref. 4) yield metallization pressures in excess of 93 and 100 GPa, as shown by the dashed curves. The extrapolation by Knittle and Jeanloz is indistinguishable from the latter, which is quantitatively confirmed by our new FTIR results.

light at about 53 GPa, in accord with previous observations.¹² No further color changes were observed in the sample at higher pressures. Our results are plotted, along with previous data, in Fig. 2. To within the accuracy of the data, there is a continuous decrease in the energy of the absorption edge with pressure, and the band-gap energy appears to be unaffected by high-pressure distortions from a cubic structure.^{2,3,13-15}

In previous studies, the spectroscopically determined pressure dependence of the absorption edge has been extrapolated as a function of either pressure or volume²⁻⁵ to obtain a metallization pressure in the range of 93 to 110 GPa. Theoretical calculations^{16,17} arrive at similar values for the pressure at which the valence and conduction bands in CsI are expected to overlap. Our FTIR measurements significantly extend the previous data, confirming that the band gap

(absorption-edge energy) vanishes above 100 GPa. This is confirmed by our observation that a sample at 98-GPa peak pressure (average pressure of 95 GPa) did not exhibit any metallic reflectivity at visible wavelengths (see Fig. 2).

Contrary to the recent claim of Vohra *et al.*⁶ CsI does not become metallic at a pressure of 65 GPa. Indeed, we find this salt to be a good mid-infrared window, and hence a useful sample matrix and pressure medium for infrared-absorption studies, to pressures exceeding 80 GPa. Furthermore, our experiments demonstrate that FTIR absorption measurements can be usefully carried out at pressures in the megabar (100 GPa) range.

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